

MANFRED T. REETZ ET AL.
USSN 09/831,566
REPLY TO OFFICE ACTION DATED JANUARY 12, 2005
AMENDMENT OF JANUARY 12, 2006

Amendments to the Specification:

Please amend page 5, first paragraph, lines 1 - 2 as follows:

- 3) Preparation of almost monodisperse nanoparticles in a size range of $0.5-5$ nm, which means a high dispersion of the metals.

Please amend page 6 last paragraph through page 7 line 13 as follows:

Amphiphilic betaines, cationic, anionic and nonionic surfactants or water soluble polymers are possible as stabilizers. Typical examples of the amphiphilic betaines are dimethyldodecylammonio propane sulfonate and dimethyldodecylammonio propane carboxylate, a typical example of the cationic surfactant is $[\text{CICH}_2\text{CH}(\text{OH})\text{CH}_2\text{N}(\text{CH}_3)_2\text{C}_{18}\text{H}_{37}]^+\text{Cl}^-$, a typical example of the anionic tenside is sodium cocoa midoethyl-N-hydroxyethyl glycinate, typical examples of the nonionic tensides are polyoxyethylenelauryl ether and polyoxyethylenesorbitanmono laurate, as well as typical examples of the water-soluble polymers are poly(vinyl pyrrolidone) (PVP), polyethylene glycol (PEG) or alkylpoly glycoside. It is also possible to use chiral water-soluble stabilizers such as poly-L-aspartic acid, sodium salt. The hydrolysis and condensation, respectively, of the metal salts in a basic, aqueous environment, and in the presence of a stabilizer is performed in a range of temperature of from 20°C to 100°C , preferably between 50°C and 90°C . Water serves as a solvent and at the same time as a chemical reactant, whereby the concentration of the aqueous solutions of the colloidal metal oxides can amount up to 0.5 M, in relation to the metal. However, mixtures of solvents, consisting of water and water-soluble organic

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solvent, can also be used.

The particle size of the nanostructured metal-oxide colloids is normally between 0.5 nm and 5 nm.

Please amend page 8, Example 1 as follows:

Example 1. PtRuO_x(3.12-SB)

370 mg (5 mmole) of Li₂CO₃ was weighed in a 250 ml three-necked flask and dissolved in 40 ml of deionized water. 40 ml of a 0.1 M solution of dimethyldodecylammonio propane sulfonate (3-12-SB) in deionized water was added thereto. A solution of 517.9 mg (1 mmole) of H₂PtCl₆ x 6 H₂O and 235.9 mg (1 mmole) of RuCl₃ x H₂O in 20 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 1 hour. Hereby, the pH value of the surfactant solution decreased from initially 11.5 to a value of 8.0, after the addition of the solution of the metal salt was completed. The solution was tempered to 60 °C and stirred at this temperature for ca. 20 hours. The progress of the hydrolysis and of the condensation was followed by UV spectroscopy by means of the decrease of the H₂PtCl₆ absorption at 260 nm. After this

Please amend page 9, second paragraph as follows:

Metal content: 10.70 % Pt, 5.82 % Ru (this is corresponding to a molar ratio of $0.95:1$)

TEM micrographs of the solution of the colloidal metal oxide solution show particles having a size distribution of 1.5 ± 0.4 nm. A individual-particle-EDX- analysis of these particles indicates bimetal character, since both metals always can be detected in a molar ratio between 1:2 and 2:1.

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Please amend page 10, Example 2 as follows:

Example 2. PtRuO_x(1-12-CB)

370 mg (5 mmole) of Li₂CO₃ were weighed in a 250 ml three-necked flask and dissolved in 20 ml of deionized water. 60 ml of a 0.71 M solution of dimethyldodecylammonio acetate (1-12-CB) in deionized water was added thereto. A solution of 517.9 mg (1 mmole) of H₂PtCl₆ x 6 H₂O and 235.9 mg (1 mmole) of RuCl₃ x H₂O in 20 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 1 hour. Hereby, the pH value of the surfactant solution decreased from initially 12.0 to a value of 8.5, after the addition of the solution of the metal salt was completed. The solution was tempered to 60 °C and stirred at this temperature for ca. 20 hours. The progress of the hydrolysis and the condensation were observed by UV spectroscopy by means of the decrease of the H₂PtCl₆ absorption at 260 nm. After this band had completely disappeared, the reaction was terminated and cooled to room temperature. The colloidal solution was then filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of the conductivity of the permeate was monitored conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.5 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 13.27 % Pt, 4.85 % Ru (this is corresponding to a molar ratio of 1.42:1)

TEM: 1.4 nm

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Please amend page 11 as follows:

Example 3. PtRuO_x(PVP)

370 mg (5 mmole) of Li₂CO₃ as well as 3 g of poly(vinyl pyrrolidone) (PVP) were weighed in a 250 ml three-necked flask and dissolved in 80 ml of deionized water. A solution of 517.9 mg (1 mmole) of H₂PtCl₆ x 6 H₂O and 235.9 mg (1 mmole) of RuCl₃ x H₂O in 20 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 1 hour. Hereby, the pH value of the polymer solution decreased from initially 11.5 to a value of 7.5, after the addition of the solution of the metal salt was completed. The solution was tempered to 60 °C and stirred at this temperature for ca. 20 hours. The progress of the hydrolysis and the condensation was monitored by UV spectroscopy by means of the decrease of the H₂PtCl₆ absorption at 260 nm. After this band had completely disappeared, the reaction was terminated and cooled to room temperature. Subsequently, the colloidal solution was filtered, in order to separate any precipitated metal oxide present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was monitored conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 2.9 g of a grey colloid powder was obtained which is completely re-dispersible in water, MeOH, EtOH and DMF.

Metal content: 6.78 % Pt, 3.15 % Ru (this is corresponding to a molar ratio of 1.11:1)

TEM: 1.6 nm

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Example 4. PtRuO_x (3-12-SB), Pt/Ru = 4:1

370 mg (5 mmole) of Li₂CO₃ was weighed in a 250 ml three-necked flask and dissolved in 40 ml of deionized water. 40 ml of a 0.1 M solution of dimethyldodecylammonio propane sulfonate (3-12-SB) in deionized water

Please amend page 12 as follows:

was added thereto. A solution of 828.6 mg (1.6 mmole) of H₂PtCl₆ x 6 H₂O and 94.4 mg (0.4 mmole) of RuCl₃ x H₂O in 20 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 1 hour. Hereby, the pH value of the surfactant solution decreased from initially 11.5 to a value of 8.0, after the addition of the solution of the metal salt was completed. The solution was tempered to 80 °C and stirred at this temperature for ca. 6 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the H₂PtCl₆ absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was monitored conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.2 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 14.87 % Pt, 2.97 % Ru (this is corresponding to a molar ratio of 2.59:1)

TEM: 1.5 nm

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Example 5. PtRuO_x (3-12-SB), Pt/Ru = 1:4

370 mg (5 mmole) of Li₂CO₃ was weighed in a 250 ml three-necked flask and dissolved in 40 ml of deionized water. 40 ml of a 0.1 M solution of dimethyldodecylammonio propane sulfonate (3-12-SB) in deionized water was added thereto. A solution of 207.2 mg (0.4 mmole) of H₂PtCl₆ x 6 H₂O and 377.4 mg (1.6 mmole) of RuCl₃ x H₂O in 20 ml of deionized water was added dropwise thereto at room temperature for 1 hour. Hereby, the pH value of the surfactant solution decreased from initially

Please amend page 13, Example 6 as follows:

Example 6. PtO₂ (3-12-SB)

296 mg (4 mmole) of Li₂CO₃ and 674 mg (2 mmole) of PtCl₄ were weighed in a 250 ml three-necked flask and dissolved in 160 ml of deionized water. 40 ml of a 0.1 M solution of dimethyldodecylammonio propane sulfonate (3-12-SB) in deionized water was added thereto. The solution was stirred at 80 °C for 24 hours, whereby a discoloration from yellow orange to red brown occurred. After termination of the reaction, the colloidal platinum dioxide solution was filtered, and, subsequently, the solution was dialyzed twice against 1.5 l of deionized water in a Nadir dialyzing tube. The change of conductivity of the permeate was monitored conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.3 g of a grey colloid powder was obtained which is completely re-dispersible in water.

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Please amend page 14 as follows:

Metal content: 22.41 % Pt14

TEM: 1.7 nm

Example 7. PtRuO_x-colloid having a chiral tenside as stabilizer

370 mg (5 mmole) of Li₂CO₃ was weighed in a 250 ml three-necked flask and dissolved in 20 ml of deionized water. 60 ml of a 0.1 M solution of 3(N,N-dimethyldodecylammonio-2-(S)-hydroxy butyrate (3-12-CB*) in deionized water was added thereto. A solution of 517.9 mg (1 mmole) of H₂PtCl₆ x 6 H₂O and 235.9 mg (1 mmole) of RuCl₃ x H₂O in 20 ml of deionized water was added thereto dropwise with strong stirring at room temperature for 1 hour. Hereby, the pH value of the surfactant solution decreased from initially 12 to a value of 8.0, after the addition of the solution of the metal salt was completed. The solution was tempered to 80 °C and stirred at this temperature for 26 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the H₂PtCl₆ absorption at 260 nm. After termination of the reaction; the colloidal solution was filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was followed conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.5 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 6.24 % Pt, 3.92 % Ru (this is corresponding to a molar ratio of 0.82:1)

TEM: 1.6 nm

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Please amend page 15 as follows:

Example 8. PtRuO_x-colloid having a chiral polymer as stabilizer

37 mg (0.5 mmole) of Li₂CO₃ as well as 500 mg of poly-L-aspartic acid, sodium salt were weighed in a 50 ml two-necked flask and dissolved in 10 ml of deionized water. A solution of 51.8 mg (0.1 mmole) of H₂PtCl₆ x 6 H₂O and of 23.6 mg (0.1 mole) of RuCl₃ x H₂O in 5 ml of deionized water was added dropwise thereto with strong stirring over a period of 10 minutes at room temperature. Hereby, the pH value of the polymer solution decreased from initially 11.5 to a value of 7.5 after the addition of the solution of the metal salt was completed. The solution was tempered to 60 °C and stirred at this temperature for 26 hours. The progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the H₂PtCl₆ absorption at 260 nm. After this band had completely disappeared, the reaction was terminated and cooled to room temperature. Subsequently, the colloidal solution was filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was followed conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 500 mg of a grey colloid powder was obtained which is completely re-dispersible in water, MeOH, EtOH and DMF.

Metal content: 3.78 % Pt, 1.98 % Ru (this is corresponding to a molar ratio of 0.98:1)

TEM: 1.6 nm

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Example 9. PtSnO_x (3-12-SB)

74 mg (1 mmole) of Li₂CO₃ as well as 103.6 mg (0.2 mmole) of H₂PtCl₆ x 6 H₂O were weighed in a 100 ml three-necked flask, and the solution was dissolved in 20 ml of a 0.1 M solution of dimethyldodecylammonio-

Please amend page 16 as follows:

propane sulfonate (3-12-SB) in deionized water. A solution of 37.8 mg (0.2 mmole) of SnCl₂ x 2H₂O in 5 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 30 minutes. The solution was tempered to 70 °C and stirred at this temperature for 10 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the H₂PtCl₆ absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 0.5 l of deionized water. The change of conductivity of the permeate was followed conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 0.6 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 6.79 % Pt, 2.67 % Sn (this is corresponding to a molar ratio of 1.55:1)

TEM: 1.5 nm

The EDX analysis of the particles indicates a bimetal character.

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Example 10. PtFeO_x (3-12-SB)

74 mg (1 mmole) of Li₂CO₃ as well as 103.6 mg (0.2 mmole) of H₂PtCl₆ x 6 H₂O were weighed in a 100 ml three-necked flask, and the solution was dissolved in 20 ml of a 0.2 M solution of dimethyldodecylammoniopropyl sulfonate (3-12-SB) in deionized water. A solution of 39.8 mg (0.2 mmole) of FeCl₂ x 4 H₂O in 5 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 30 minutes. The solution was tempered to 70 °C and stirred at this temperature for 10 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the

Please amend page 17 as follows:

decrease of the H₂PtCl₆ absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide possibly present, and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 0.5 l of deionized water. The change of conductivity of the permeate was followed conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 0.6 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 6.12 % Pt, 1.24 % Fe (this is corresponding to a molar ratio of 1.42:1)

TEM: 1.5 nm

The EDX analysis of the particles indicates a bimetal character.

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Example 11. PtWO_x (3-12-SB)

74 mg (1 mmole) of Li₂CO₃ as well as 103.6 mg (0.2 mmole) of H₂PtCl₆ x 6 H₂O were weighed in a 100 ml three-necked flask, and the solution was dissolved in 20 ml of a 0.1 M solution of dimethyldodecylammonio propane sulfonate (3-12-SB) in deionized water. A solution of 66.0 mg (0.2 mmole) of Na₂WO₄ in 5 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 30 minutes. The solution was tempered to 70 °C and stirred at this temperature for 10 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the H₂PtCl₆ absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered, in order to separate any precipitated metal oxide present and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 0.5 l of deionized water. The change of conductivity of the permeate was followed conductometrically.

Please amend page 18, Example 12 as follows:

Example 12. PtRuWO_x (3.12-SBI)

370 mg (5 mmole) of Li₂CO₃ was weighed in a 250 ml three-necked flask and dissolved in 20 ml of deionized water. 60 ml of a 0.1 M solution of dimethyldodecylammonio propane sulfonate (3-12-SB) in deionized water was added thereto. A solution of 517.9 mg (1 mmole) of H₂PtCl₆ x 6 H₂O and 141.5 mg (0.6 mmole) of RuCl₃ x H₂O and of 66.0 mg (0.2 mmole) of Na₂WO₄ in 20 ml of deionized water was added dropwise thereto with strong stirring at room temperature for 3 hours. Hereby, the pH value of the tenside solution decreased from initially 11.4 to a value of 9.8,

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after the addition of the solution of the metal salt was completed. The solution was tempered to 60 °C and stirred at this temperature for ca. 22 hours, whereby the progress of the hydrolysis and the condensation was followed by UV spectroscopy by means of the decrease of the H_2PtCl_6 absorption at 260 nm. After termination of the reaction, the colloidal solution was filtered and submitted to an dialyzing process. Hereby, the colloidal solution of the metal oxide was filled into a Nadir dialyzing tube and dialyzed twice against 1 l of deionized water. The change of conductivity of the permeate was followed conductometrically. Thereafter, the solution was filtered once again, and the colloidal solution was lyophilized. 1.8 g of a grey colloid powder was obtained which is completely re-dispersible in water.

Metal content: 8.31 % Pt, 2.91 % Ru, 0.73 % W

Please amend page 19, second paragraph as follows:

TEM micrographs of the colloidal solution of PtRu show particles having a size distribution of 1.7 ± 0.4 nm. A EDX individual particle analysis of these particles indicates an almost complete formation of an alloy.

XPS examinations with these colloids showed that both platinum and ruthenium are present in a metallic form.

Please amend page 20, Example 15, as follows:

Example 15: Fixation of a PtRuO_x colloid on Vulcan as the solid support

3.552 g Vulcan XC-72R of the Cabot Company which previously was surface oxidized with a solution of NaOCl was weighed in a 1 l three-necked flask and suspended in 200 ml of water. Then, 300 ml of an aqueous solution of PtRuO_x (3-12-SB) (888 mg of noble metal) prepared

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according to specification of example 1 was added dropwise thereto at 60 °C for 3 hours. Then, 0.1 M HCl was added dropwise there, until the solution reached a pH value of 2.5, and the suspension was stirred at 50 °C for 40 hours. After cooling, the black suspension was centrifuged, the supernatant solution was decanted, the catalyst was washed twice with 200 ml of methanol, respectively, and dried in vacuum at 40 °C.

Metal content: 14.32 % Pt, 8.45 % Ru

Please amend page 21, Example 19 through page 22, as follows:

Example 19: Immobilization of a PtRuO_x colloid in sol-gel-materials

1.2 ml (8 mmole) of tetramethoxy silane (TMOS) was initially added to a 2 ml polypropylene vessel, and 0.5 ml of an aqueous solution of a PtRuO_x (3-12-SB) colloid (10 mg of noble metal; 20 g/l), prepared according to the specification of example 1, and 50 µl of a 0.1 M solution of NaF was pipetted thereto. Subsequently, the vessel was sealed and agitated on a Vortex mixer at room temperature for 10 seconds. After a heating up has become evident, the black mixture was allowed to stand, whereupon a gelation of the solution occurred ca. 10 seconds later. Now, the gel was submitted to an ageing process in a sealed vessel at room temperature, for 24 hours and then dried at 37 °C in a drying oven for 3 days. To wash out the stabilizer, the gel was refluxed in 30 ml of ethanol for 3 days, centrifuged and washed again with 30 ml of ethanol, centrifuged again and finally dried in a drying oven at 37 °C for 4 days. 630 mg of a grey powder is obtained.

Metal content: 0.92 % Pt, 0.56 % Ru